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(54) Process for the selective hydrogenation of triglyceride oils with a metallic catalyst in the presence of a diamine and compound obtained.

(57) Unsaturated fatty acid derivatives which, besides fatty acids with two double bonds, contain fatty acids with more than two double bonds, are hydrogenated in the presence of a palladium, platinum or rhodium catalyst which has been treated with ethylenediamine or a homologue and/or a derivative thereof and at a temperature of -20 to 100°C. The hydrogenation progresses very selectively while very little isomerisation to trans-fatty acids occurs.

For example, in the hydrogenation of soya bean oil to a linolenic acid content of 2%, the linoleic acid content only decreases to 45-52%. Under identical conditions an untreated catalyst leads to a linoleic acid content of about 35%.

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"Process for the selective hydrogenation of triglyceride oils with a metallic catalyst in the presence of a diamine"

The invention relates to a process for the selective hydrogenation of polyunsaturated fatty acid derivatives, such as triglycerides, which, besides fatty acid with two double bonds, contain fatty acids with more than two double bonds.

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As is generally known, oils and fats consist mainly of a mixture of triglycerides of fatty acids. The fatty acids usually contain about 16 to about 22 carbon atoms and may be saturated, e.g. stearic acid; mono-unsaturated, e.g. oleic acid; di-unsaturated, e.g. linoleic acid; or tri-unsaturated, e.g. linolenic acid; or may even be unsaturated to a greater degree.

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In the field of technology relating to oils and fats it is usual to hydrogenate oils in order to remove the unsaturation partly, a hydrogenated oil being obtained having the desired properties, such as a higher melting point and/or increased stability.

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During the hydrogenation a number of reactions take place, both successively and simultaneously. Accordingly, for example, in the hydrogenation of linolenic acid the hydrogenation reactions can be represented by the following simplified scheme:

$$\text{linolenic acid} \xrightarrow{K_1} \text{linoleic acid} \xrightarrow{K_2} \text{oleic acid} \xrightarrow{K_3} \text{stearic acid},$$

the speed constants of the reactions being indicated with K_1 , K_2 , etc. Moreover, side reactions occur, such as displacement and isomerisation of double bonds. Isomerisation gives rise to the conversion of cis-double bonds into trans-double bonds, the corresponding oils which contain the trans-acids usually having a higher melting point. Oils and fats which have a high content of stearic acid have a melting point that for most applications is too high to be organoleptically acceptable. Formerly it was therefore usual to direct the hydrogenation in such a way that as little stearic acid was formed as possible, but a high content of trans-oleic acid was still obtained, so that the oil had the desired melting point. Nowadays it is considered less desirable to apply cis-trans isome-

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risation since there is a displacement involved to liquid, though stable oils, which are used as such or serve as components for soft margarines which are stored in the refrigerator.

- 5 The selectivity values of the hydrogenation reactions are usually defined as follows:

$$S_I = \frac{K_2}{K_3}$$

$$S_{II} = \frac{K_1}{K_2}$$

- 10 When the S_I value of the reaction is high, small amounts of saturated acids are obtained. With a high S_{II} value it is possible to hydrogenate linolenic acid and still retain a high percentage of the essential fatty acid: linoleic acid. With the isomerisation-selectivity value, abbreviated to S_i , the amount of trans-isomers is indicated that is formed in relation to the degree of hydrogenation. As was already observed, it is wanted at present that hydrogenation be influenced in such a way that the S_i value is as low as possible.

- 20 However, according to the current practice with hydrogenation, that is usually carried out at a high temperature and under increased pressure with the aid of a nickel catalyst supported on a carrier, a not unimportant isomerisation of double bonds cannot be avoided.

- 25 The use of some catalysts, for example copper catalysts, has been proposed on account of their higher selectivity. Although it is true that such catalysts are more selective, the degree of isomerisation they bring about is, however, about the same as that of nickel.

- 30 The use of palladium catalysts has been proposed for the selective hydrogenation of soya oil (Belgian patent specification 851,202). Although these catalysts are selective, the content of linoleic acid obtained with them is not higher than 40% at a linolenic acid content of 2% when a soya oil containing 7-9% of linolenic acid and 50-55% of linoleic acid is used as starting material.
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According to Belgian patent specification 872,476 triglyceride oils

are hydrogenated, using a nickel catalyst, which has been treated with a basic nitrogen compound, including hexamethylene tetramine, the molar ratio nitrogen : nickel being about 0.05-0.4:1.

- 5 According to Belgian patent specification 872,477 the hydrogenation of triglyceride oils is carried out, using a nickel catalyst in the presence of a basic nitrogen compound, in which the molar nitrogen:nickel ratio is about 0.05-0.4:1.
- 10 According to the last two patent specifications the hydrogenation is carried out at a temperature of 100 to 175°C. Also according to the last-mentioned two processes in the hydrogenation of soya oil to a linolenic acid content of 2%, linoleic acid contents are obtained lower than 40%, the transisomer content in the hydrogenated
- 15 product being about 15 to 20%.

It has now been found, surprisingly, that very high selectivity values, particularly a high S_{II} value, are obtained in the hydrogenation of poly-unsaturated fatty acid derivatives which, besides

20 fatty acids with two double bonds, contain fatty acids with more than two double bonds, when the hydrogenation is carried out in the presence of palladium, platinum and/or rhodium as catalyst, if the catalyst is treated with ethylenediamine (1,2-diamino ethane) or a homologue and/or derivative thereof, in a molar ratio of the number

25 of nitrogen atoms to the catalytically active metal of at least 100:1 and the hydrogenation is carried out at a temperature of -20 to 100°C.

It has already been proposed earlier to carry out the hydrogenation

30 of edible oils in the presence of additives, such as alcohols and polyalcohols (see British patent specification 1,080,891) or amines (Japanese patent specification 4021/62), but with the process according to the present application higher selectivity values are obtained.

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It has now been found that with the process according to the invention hydrogenation is influenced in such a way that a selective

hydrogenation of polyunsaturated fatty acid groups takes place without any formation of saturated fatty acid groups at all, while relatively few trans-isomers are formed. Moreover, the invention is characterized in that linolenic acid groups (or trienoic acid groups) if present are hydrogenated more readily than dienoic acid (linoleic acid) groups, with the result that products are formed which have a low content of linolenic acid and a high content of linoleic acid.

10 The catalyst may contain a so-called promotor, i.e. a metal that promotes the effect of the catalyst with respect to its activity and/or selectivity, such as Cu, Ag, Zu, Zn, Sn, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W or Mn.

15 The catalyst can be used in the form of a porous metal supported on a carrier in sheet form that is immersed in the system, or preferably in the form of small particles, such as palladium powder, suspended in the system. The metallic component can be supported on a carrier. Carbon, silicon dioxide, aluminium dioxide, kieselguhr
20 or an ion-exchange resin can, for example, be used as carrier for the catalyst.

The amount of catalytically active material used for the hydrogenation is not critical and can vary from 1 mg/kg to 10 g/kg, calculated
25 on the basis of the metal with respect to the compound to be hydrogenated, as the amount is dependent on the form of the catalyst, whether supported on a carrier or not, on the massive surface area of the catalyst, on the catalytic activity of the metal used, on the amount of diamine added, and on other factors.

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The catalyst can be treated with the diamine before the hydrogenation reaction, and this mixture, either as such or after the excess diamine has been removed by decantation, can be added to the material to be hydrogenated. In the pre-treatment of the catalyst, water or an
35 organic liquid such as acetone, tetrahydrofuran, dimethylformamide, or alcohols and polyalcohols or a mixture thereof can be used as liquid.

The diamine can also be added direct to the compound to be hydrogenated, and then preferably dissolved in one of the above-mentioned solvents. When this method is followed, the treatment of the catalyst with the diamine takes place in situ.

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The amount of diamine is such that at least 100 nitrogen atoms per atom of the catalytically active metal are present. As a result of this a high selectivity of the hydrogenation is ensured. For example, in the hydrogenation of soya oil which contains about 55% of linoleic acid and 7% of linolenic acid, the amount of linolenic acid can be reduced to 2%, the linoleic acid content remaining higher than 40%, i.e. at least 70% of the original linoleic acid is retained. Often even more than 80% and even more than 90% of the linoleic acid is retained. The activity, the selectivity and the formation of trans-isomers depend on the amount of diamine that is added. If this amount is increased, this usually leads to a slighter activity and to a better selectivity and slighter cis-trans isomerisation.

20 The ratio of the number of nitrogen atoms to the catalytically active metal is generally not higher than 5,000:1, preferably 2,000:1.

25 The activity, selectivity and the formation of trans-isomers effected during hydrogenation with the addition of a certain amount of diamine are dependent on the amount and the type of catalyst. When a triglyceride is hydrogenated, the quality of the oil and the refining process of the raw oil influence the hydrogenation characteristics when different amounts of diamines are added.

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Besides ethylenediamine itself, also homologues and/or derivatives hereof can be used. Examples of such homologues and derivatives are: diethylenediamine (piperazine or perhydro-1,4-diazine), triethylenediamine (1,4-diazabicyclo[2.2.2] octane), diethylenetriamine (1,4,7-triazaheptane), hexamethylenetetramine and suchlike; 1,2-diaminopropane, 1,3-diaminopropane, and suchlike. Compounds of primary, secondary or tertiary amino groups also yield excellent results.

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Examples of such compounds are: N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylhexanediamine, N,N,N',N'-tetramethyldiethylenetriamine, N,N-dimethyl-1,3-propanediamine, etc. Oligoamines or polyamines, such as 4,7,11-triazatetradecane-1,14-diamine, can also be used.

When the process according to the invention is being carried out, the compound to be hydrogenated can be dissolved or dispersed in an organic liquid such as a ketone or a hydrocarbon. Good results are also obtained with alcohols, though in that case alcoholysis or interesterification can occur; so, if alcoholysis or interesterification is desired, alcohols can then be used.

The ratio of liquid to substrate is not critical and can vary from an amount that is just necessary to dissolve the diamine and to keep the catalyst in suspension up to about 20:1.

The hydrogenation can also be carried out in the pure compound, while the added diamine is dissolved in water or an organic liquid.

The process is not sensitive to the presence of water, although the amount of water should be limited to a minimum, so that as little loss of oil as possible takes place because of saponification of the ester or that separation of the catalyst/substrate mixture occurs.

Generally the hydrogenation is carried out in a suitable apparatus, such as a reaction vessel with a stirrer, or continuously in a series of reaction vessels with stirrer, though good results can also be obtained when the hydrogenation takes place over a column of catalyst particles. The hydrogenation can be carried out by adding the diamine and the catalyst to the substrate under nitrogen or another inert gas and starting the hydrogenation reaction by addition of hydrogen, or the substrate can be introduced into the reaction vessel in which the diamine or a pretreated catalyst is present under a hydrogen atmosphere. The catalyst can first be treated with the diamine and added to the hydrogenation reactor,

or the excess diamine can be removed by centrifuging or filtering and washing, whereafter the treated catalyst is introduced into the hydrogenation reactor in which the substrate to be hydrogenated is present.

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The temperature at which the hydrogenation is carried out is preferably 0°C to 60°C.

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The reaction can be carried out under atmospheric pressure or under higher pressure; generally the pressure will vary from 100 to 2500 kPa. Naturally, if it is desired to work at a temperature above the boiling point of any liquid used, a pressure above atmospheric pressure should be applied.

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The process can be regulated in a known manner, for example by stopping the hydrogenation when a previously calculated amount of hydrogen has been absorbed.

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The process according to the invention can be applied for the hydrogenation of compounds or groups which contain more than one double bond in order to increase the selectivity of the hydrogenation reaction. Examples that can be mentioned are the hydrogenation of soya oil, rapeseed oil, linseed oil, fish oils, tallow and similar animal fats, esters of fatty acids, such as the methyl-, ethyl- and other alkylesters, soaps, alcohols and other fatty acid derivatives in which the hydrogenation plays an important role.

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The products can be used as deep-frying oil, table oil, as raw material for margarine or as raw material for the preparation of stable products such as soaps, esters, etc.

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The invention is further illustrated by means of the following Examples. In some Examples the sum of the amounts of components does not add up to 100%, as less important fatty acid components, such as C₁₄-, C₁₇-, C₂₀- and C₂₂-fatty acids, are not mentioned. The composition of the substrates before and after hydrogenation is given in mol.%.



In the Tables the fatty acids are designated by the number of carbon atoms present therein and the number of double bonds, that is to say C18:3 means linolenic acid and isomers, C18:2 means linoleic acid and isomers, etc.

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Example I

The hydrogenation was carried out under atmospheric pressure and at room temperature in an apparatus consisting of a vessel with a net volume of 100 cm³ and provided with a magnetic stirrer, four
10 baffle plates, an inlet for hydrogen, an inlet for substrate and a device for drawing off samples.

The reactor was connected with a 500 cm³ calibrated burette filled with hydrogen (purified over a copper catalyst (BTS) and a molecular
15 sieve) and paraffin oil. The reactor was loaded with 60 mg palladium on carbon (3%) as catalyst and 70 ml acetone. The reactor was repeatedly evacuated and purged with argon. The solution was stirred and 1 ml ethylenediamine added. Subsequently the argon was replaced by hydrogen. After 15 minutes 25 g oxygen-free soya oil was added.

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At fixed intervals samples were drawn off for determination of the fatty acid composition by GLC and the trans content by IR, as is shown in Table A.

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TABLE A

Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (%)
	C16:0	C18:0	C18:1	C18:2	C18:3	
30 Starting oil	10.8	3.9	23.4	54.7	7.2	-
70	10.8	3.6	31.6	51.3	2.6	6
110	10.8	3.6	35.6	48.3	1.6	7
155	10.8	3.8	41.0	43.8	0.7	8

35 In a comparative test in which no diamine was present but otherwise under the same conditions, the following result was obtained:

Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (%)
	C16:0	C18:0	C18:1	C18:2	C18:3	
8	10.7	5.0	46.5	35.5	2.0	12

Example II

Example I was repeated, with the exception that other additives, such as indicated in Table B, were used. The fatty acid composition at 2% C18:3 was determined by interpolation.



TABLE B

Selective hydrogenation of soya oil with palladium-on-carbon catalyst (3%) in a medium consisting of acetone with various organic nitrogen compounds as additive.
Conditions: 60 mg Pd/C (3%), 70 ml acetone, 25 g soya oil.

Additive	Fatty acid composition (mol.%)						Trans (%)	Reaction time (min.)
	mmol	C16:0	C18:0	C18:1	C18:2	C18:3		
Starting oil	-	10.8	3.9	23.4	54.7	7.2		
Ethylenediamine	15	11.0	3.6	33.5	49.5	2.0	6	90
Diethylenediamine (piperazine)	2	11.0	3.7	34.0	49.5	2.0	6	43
Triethylenediamine	2	11.0	3.7	35.0	48.0	2.0	6	28
Diethylenetriamine	1	10.6	4.0	37.0	46.2	2.0	7	45
N,N,N',N'-tetramethylenediamine	6	11.0	4.0	37.0	46.0	2.0	7	25
N,N,N',N'-tetramethylhexanediamine	2	11.0	4.0	37.3	45.3	2.0	7	27
Hexamethylenetetramine	2	10.8	3.8	37.7	45.8	2.0	7	20
1,2-diaminopropane	6	11.0	4.0	35.0	47.0	2.0	6	31
1,3-diaminopropane	10	11.0	3.6	33.5	49.0	2.0	5	80
N,N-dimethyl-1,3-propanediamine	7	10.8	4.0	36.0	47.0	2.0	7	33

Example III

Example I was repeated, with the exception that another solvent was used, as indicated in Table C.

TABLE C

Solvent	Additive (mmol)	Fatty acid composition (mol.%)					Trans (%)	Reaction time (min.)
		C16:0	C18:0	C18:1	C18:2	C18:3		
Ethyl-acetate	Piper-azine (1)	10.8	3.6	35.0	49.5	2.0	6	80

Example IV

The reaction was carried out in a reaction vessel with thermostat, and with the same provisions as according to Table A. The reactor was loaded with 200 mg palladium on carbon (3%) and 35 g soya oil. The temperature was adjusted to 40°C and the stirring was started. The reactor was repeatedly evacuated and purged with argon. Subsequently 0.05 cm³ ethylenediamine was added. The argon was replaced by hydrogen and the hydrogenation was started. The results are shown in Table D.

TABLE D

Hydrogenation time (min.)	Fatty acid composition (mol.%)					Trans (%)
	C16:0	C18:0	C18:1	C18:2	C18:3	
Starting oil						
80	10.7	3.7	30.4	52.7	2.4	7
120	10.8	3.6	34.2	50.2	1.3	10

C L A I M S

1. A process for the selective hydrogenation of unsaturated fatty acid derivatives, which, besides fatty acids with two double bonds, contain fatty acids with more than two double bonds, in the presence of a catalytically active metal of group VIII of the periodic system of the elements which as promotor can contain a metal of the same or another group of the periodic system, and has been treated with a nitrogen compound, characterized in that as catalytically active metal Pd, Pt and/or Rh is used, which has been treated with ethylenediamine or a homologue and/or derivative thereof in a molar ratio of the number of nitrogen atoms to the catalytically active metal of at least 100:1, and the hydrogenation is carried out at a temperature of -20 to 100°C.
2. A process according to claim 1, characterized in that the catalyst is treated with the diamine before it is added to the compound to be hydrogenated.
3. A process according to claim 2, characterized in that the excess diamine is separated from the catalyst before the catalyst is added to the compound to be hydrogenated.
4. A process according to claim 1, characterized in that the diamine is added direct to the compound to be hydrogenated.
5. A process according to claims 1 to 4, characterized in that the diamine is dissolved in water or an organic liquid or a mixture thereof.
6. A process according to claims 1 to 5, characterized in that diethylenediamine is used.
7. A process according to claims 1 to 5, characterized in that triethylenediamine is used.
8. A process according to claims 1 to 5, characterized in that diethylenetriamine is used.

9. A process according to claims 1-5, characterized in that N,N,N',N'-tetramethylethylenediamine is used.
- 5 10. A process according to claims 1 to 5, characterized in that N,N,N',N'-tetramethylhexanediamine is used.
11. A process according to claims 1 to 5, characterized in that hexamethylenetetramine is used.
- 10 12. A process according to claims 1 to 5, characterized in that 1,2-diaminopropane is used.
13. A process according to claims 1 to 5, characterized in that 1,3-diaminopropane is used.
- 15 14. A process according to claims 1 to 5, characterized in that N,N-dimethyl-1,3-propanediamine is used.
- 20 15. A process according to claims 1 to 14, characterized in that the compound to be hydrogenated is dissolved in an organic liquid, preferably a ketone, hydrocarbon, alcohol or a mixture thereof.
- 25 16. A process according to claims 1 to 14, characterized in that the hydrogenation takes place without addition of a solvent for the compound to be hydrogenated.
- 30 17. A process according to claims 1 to 16, characterized in that the hydrogenation reaction is carried out at a temperature of 0° to 60°C.
18. A process according to claims 1 to 17, characterized in that the hydrogenation is carried out under a pressure of 100 to 2500 KPa.
- 35 19. A process according to claims 1 to 18, characterized in that the compound to be hydrogenated is an edible triglyceride oil.



20. A compound hydrogenated by application of a process according to claims 1 to 19.





European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 80 20 0576

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	BE - A - 872 476 (LABOFINA SA) * Page 3, paragraphs 2-5; page 4, paragraphs 2-3; page 5, paragraph 3; example 1 *	1-3, 12, 17- 20	C 11 C 3/12 B 01 J 31/28
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D	BE - A - 872 477 (LABOFINA SA) * Page 3, paragraphs 2-4; page 4, paragraph 2; page 4, paragraph 4 - page 5, paragraph 3; example III *	1-4, 12, 17- 20	
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AD	BE - A - 851 202 (JOHNSON, MATTHEY & CO)		
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A	CHEMICAL ABSTRACTS, vol. 59, no. 7, 30-09-1963, column 7762c Columbus, Ohio, US & JP - A - 4021 (AJINOMOTO CO. INC.) (11-06-1962)		C 11 C 3/12 B 01 J 31/28 23/40 23/42 23/44 23/46 C 01 B 7/00

			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 11 C 3/12 B 01 J 31/28 23/40 23/42 23/44 23/46 C 01 B 7/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	25-09-1980	SCHUERMANS	